Development of Improved Accelerated Corrosion Qualification Test Methodology for Aerospace Materials

18-20 Nov 2014

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Outline

- Motivation for effort/background
- Aircraft organic coating failure mechanisms
- State of the art corrosion testing and characterization of organic coatings- deficiencies
- AFRL efforts to address gaps:
  - AFRL SERDP project
  - SBIRs
  - AFRL in-house program, “Structural Component Corrosion Simulation”
- Conclusions

Motivation/Background

- **Weapon system corrosion performance requirements:**
  - **New acquisition–design, intended environment and expected service life taken into account**
  - **Legacy systems– field/depot maintenance, material substitution/replacement**

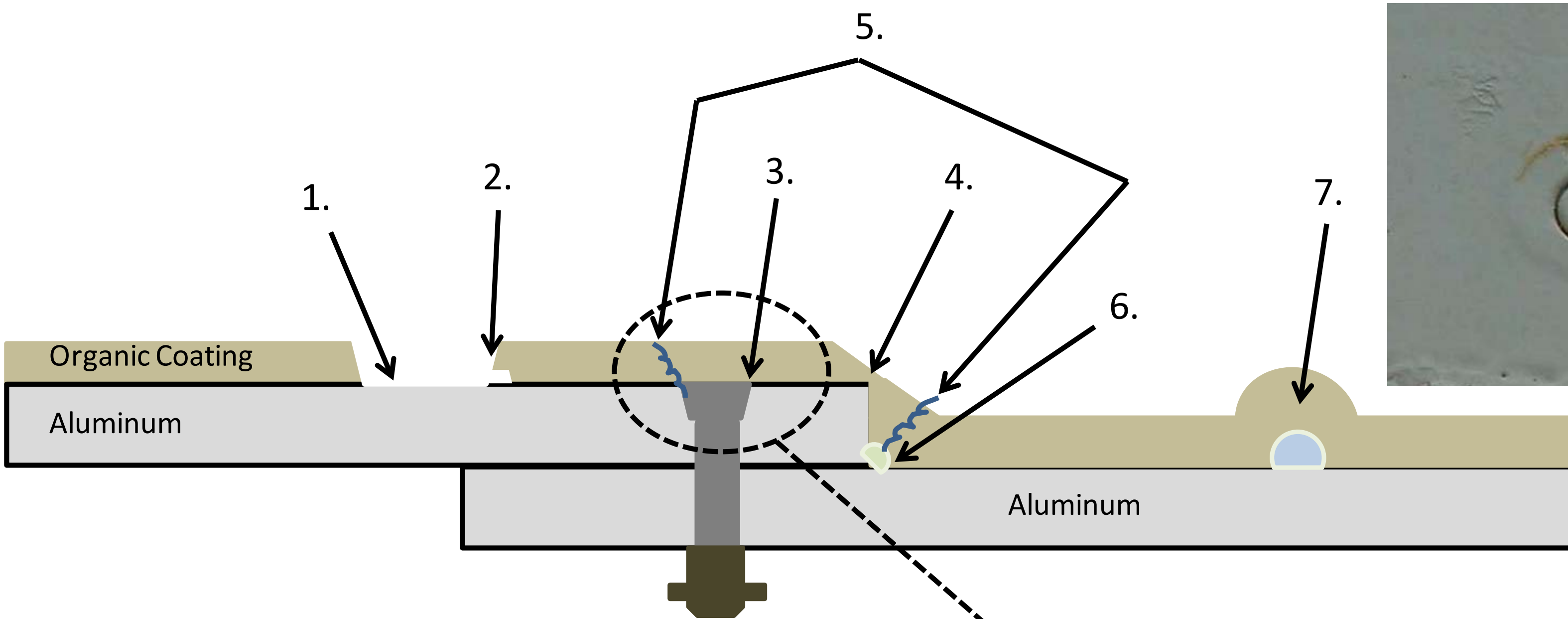
- **Driven by several synergistic factors including:**
  - **Environmental regulations and high corrosion costs (DoD-wide),**
  - **Requirement to account for corrosion in management of structures (MIL-STD-1530C, Aircraft Structural Integrity Program, Air Force-specific but approaches could apply to other services)**
  - **Improved performance**

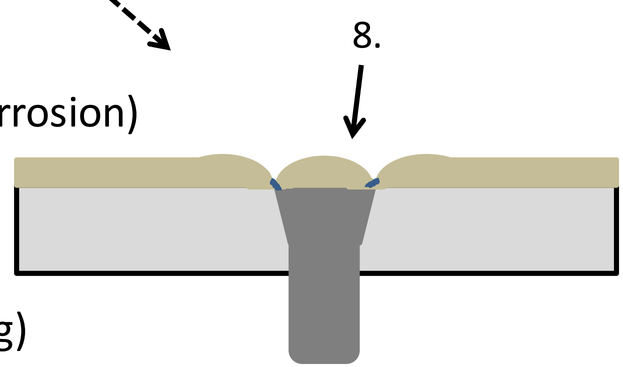
- **Current accelerated laboratory methodology inadequate to predict performance with relevant degradation modes**
- **Long-term outdoor exposure is current best practice for performance prediction, but takes 1 year+ and doesn't mimic service conditions precisely**

Background- Air Force Requirements

- MIL-STD-1530C (Aircraft Structural Integrity Program), Section 5.1.5 requires the establishment of a Corrosion Prevention and Control Program
    - 5.1.5.1 Corrosion Prevention and Control Plan
    - 5.1.5.2 Evaluation of Corrosion Susceptibility (accounting for base metals, coatings, sealants, service environments & maintenance practices, etc.)
- "Materials and processes, finishes, coatings, and films which have been proven in service *<u>or by comparative testing in the laboratory</u>* shall be selected to prevent corrosion…"
- There is currently no way to reliably meet the above criteria for emerging environmentally-compliant coatings M&P!

Coating Degradation Mechanisms





1. Mechanical defect (pitting)
2. Coating delamination (crevice corrosion)
3. Fastener/structure interface (galvanic/crevice corrosion)
4. Coating delamination (crevice corrosion/pitting)
5. Coating cracking
6. Air pocket (crevice corrosion/pitting)
7. Water-induced disbond (crevice corrosion/pitting)
8. Typical morphology of organic coating around fastener

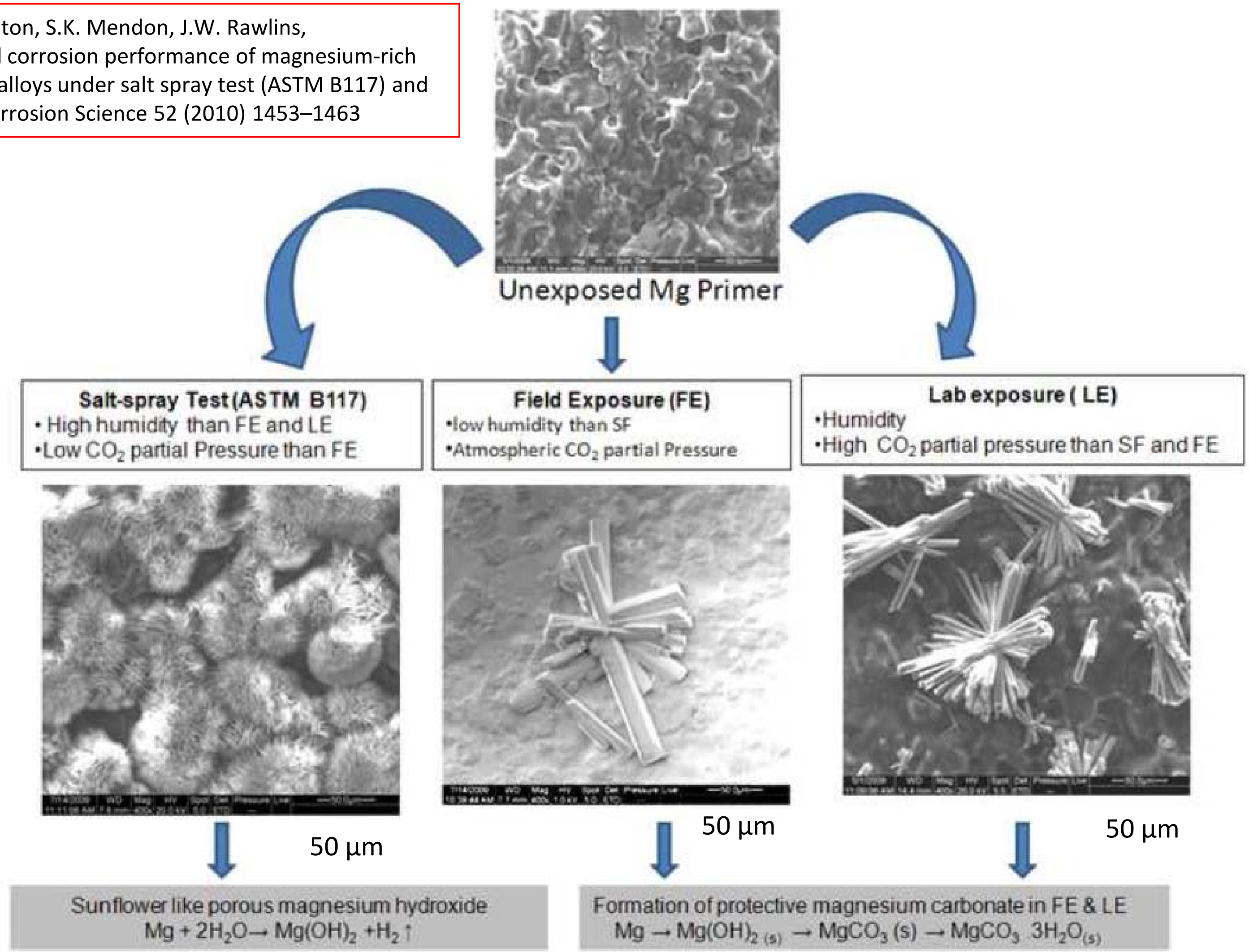
Corrosion Testing and Characterization of Organic Coatings- Deficiencies

Laboratory salt fog (ASTM B117, 5% NaCl spray at 35°C) 2000 hrs

Outdoor Exposure After 3+ Years At Daytona, FL (Failure <1 year)

Mg-rich primer degradation mechanisms

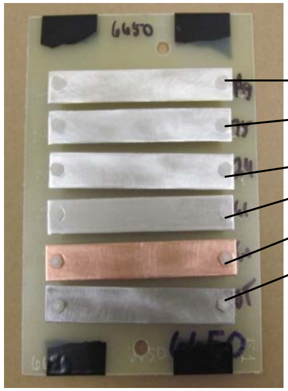
S.S. Pathak, M.D. Blanton, S.K. Mendon, J.W. Rawlins, "Investigation on dual corrosion performance of magnesium-rich primer for aluminum alloys under salt spray test (ASTM B117) and natural exposure", Corrosion Science 52 (2010) 1453–1463



AFRL SERDP Project

- AFRL project proposed against 2009 Strategic Environmental Research and Development (SERDP) Statement of Need "Dynamic Accelerated Corrosion Test Protocol"

- Bare and coated metal samples exposed:
  - At 8 outdoor test sites
  - Laboratory, ASTM B117 salt fog
  - Laboratory, ASTM B117 salt fog with UVA irradiation and ozone gas
- Cumulative damage model for predicting atmospheric corrosion rates of 1010 steel was developed using inputs from weather data:
  - Temperature,
  - Relative humidity (%RH)
  - Atmospheric contaminants (chloride, SO_2, and ozone) levels



AFRL SERDP Project - Results

- AgCl film develops on Ag coupons exposed in modified B117 lab test with UV/ozone and outdoors, much higher than what occurs in ASTM B117

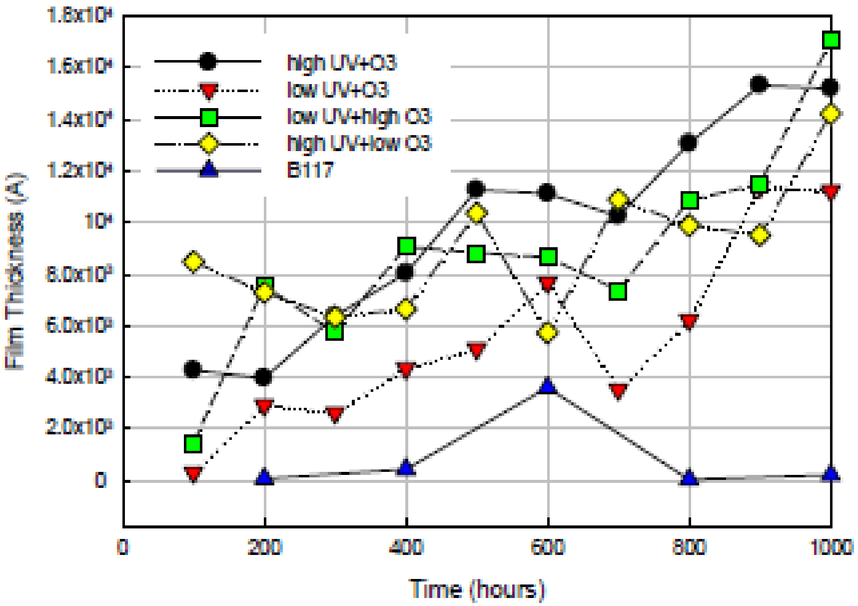


Figure 53. AgCl film thickness measurements on pure silver coupons as a function of exposure condition (UV/ozone) over 1000 hours in the modified exposure chamber and the B117 test chamber.

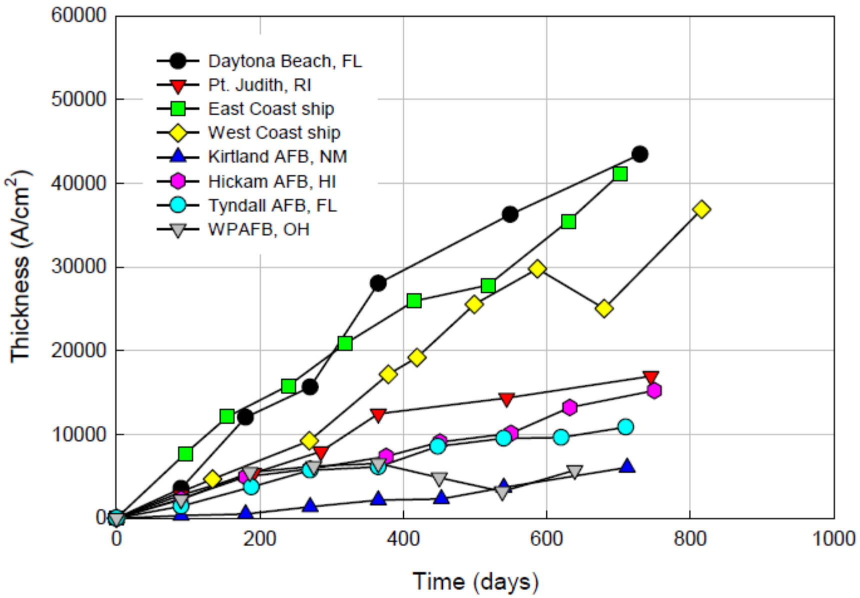


Figure 20. AgCl film thickness on pure silver coupons as a function of time over a two year period at all exposure sites.

Coulometric reduction method

AFRL SERDP Project - Results

West Coast Ship
2 Years

Pt Judith
2 Years

Low UV/High O_3
400 Hours

B117
400 Hours

Cr system

West Coast Ship
2 Years

Pt Judith
2 Years

Low UV/High O_3
400 Hours

B117
400 Hours

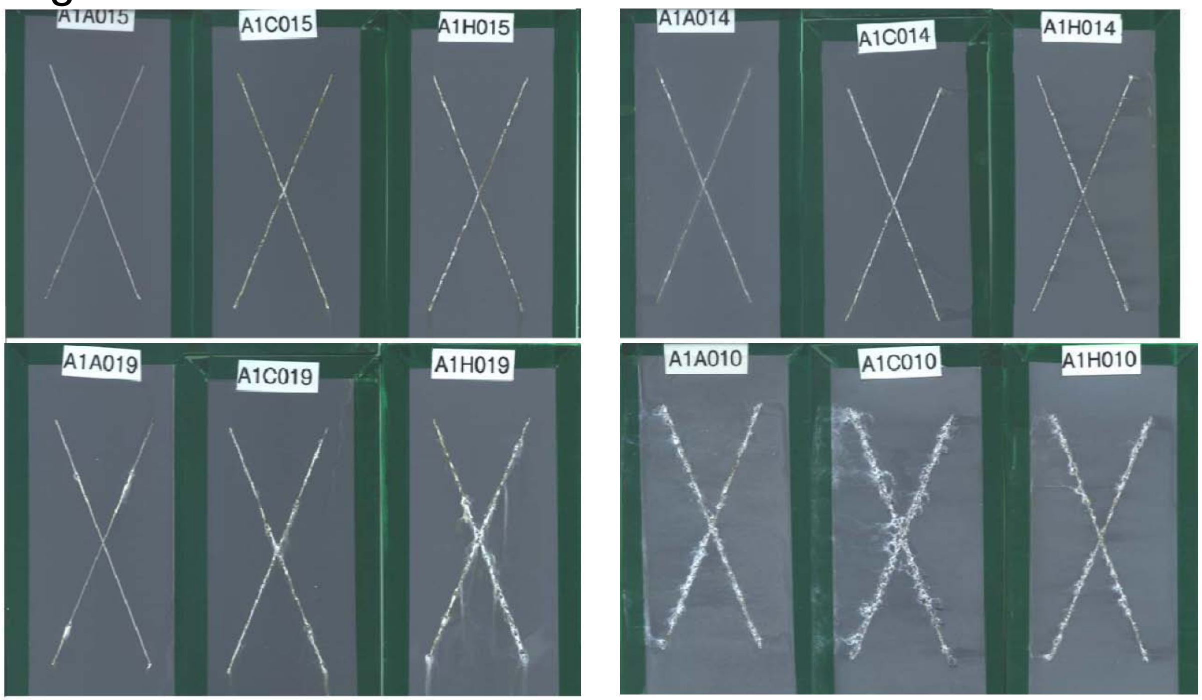
Mg rich system

AFRL SERDP Project - Results

Mg rich RE Cr Mg rich RE Cr

400 Hrs

2000 Hrs



B117 Chamber

Modified UV/ozone Chamber

Figure 60. Side-by-side chamber exposure comparison of the three coating systems on AA2024-T3 panels at (top) 400 hours and (bottom) 2000 hours exposure in the modified UV/ozone and B117 chambers, respectively. Panel coating designation code: A1A: magnesium rich coating system; A1C: rare earth conversion coat (RECC) system; A1H: full chromate coating system.

AFRL SERDP Project – Test Results

- Corrosion of coated panels in outdoor environments: strong correlation to elevated T and % RH
- Cumulative amount of time coated panel is exposed to damaging environments was dominant factor in corrosion severity
- Degradation of polyurethane topcoat observed (FTIR analysis)
- UV and ozone under constant salt fog on coated panels in laboratory was much more damaging than 2 years field exposure
- Promising results; further development of laboratory apparatus and improved methods needed

Cumulative Damage Model for Prediction of Atmospheric Corrosion

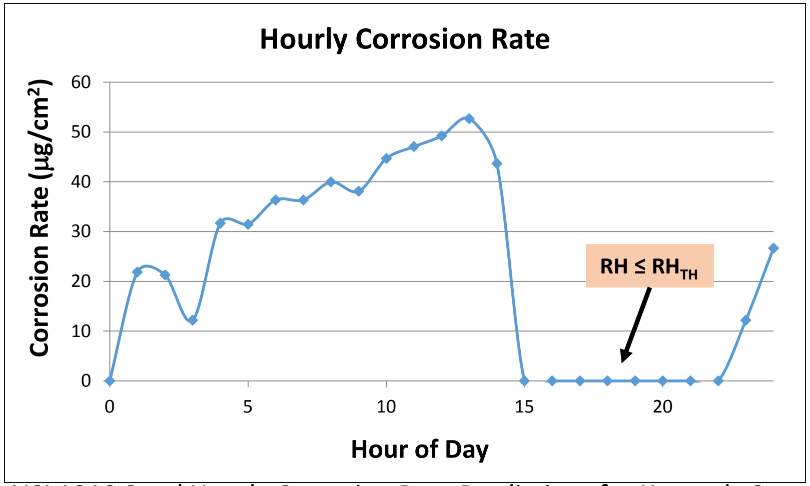
- There are 3 principal boundary conditions
  - The corrosion rate equals zero when:
    - Relative humidity drops to a threshold value, RH_{TH}
      - 60% RH for iron and steel*
    - Temperature drops to freezing or below
    - Contaminant level falls to zero
- A piecewise function is used to implement the temperature and RH boundary conditions

$$Ki = \begin{cases} f(T, RH, Cl, SO_2, O_3), & RH > RH_{TH} \text{ and } T > T_f \\ 0, & RH \le RH_{TH} \text{ or } T \le T_f \end{cases}$$

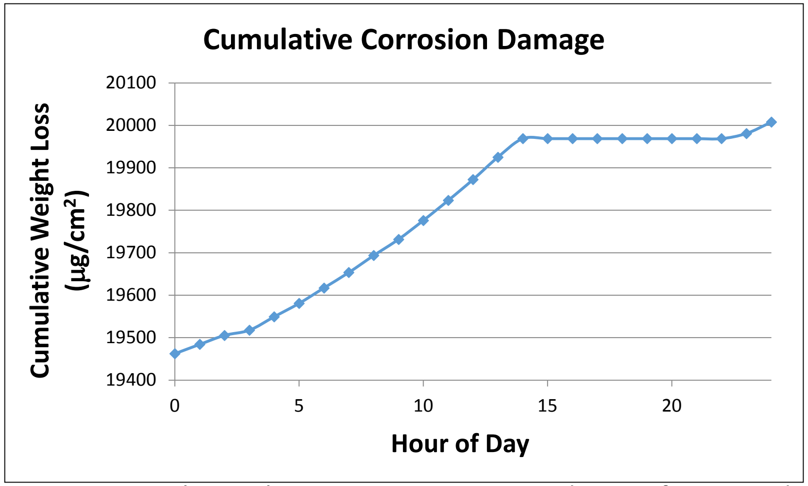
Form based on Eyring equation describing the variance of the rate of a chemical reaction with temperature

$$K_i = \overbrace{\exp\left(\frac{\Delta H}{kT}\right)}^{\text{Material Reactivity (kinetics)}} [\overbrace{A_{CL} T^{\alpha CL} f_{Cl}(T, RH) f(T, Cl)}^{\text{Chloride Reaction}} + \overbrace{A_{SO2} T^{\alpha SO2} f_{SO2}(T, RH) f(T, SO_2)}^{\text{Sulfur Dioxide Reaction}} + \underbrace{A_{O3} T^{\alpha O3} f_{O3}(T, RH) f(T, O_3)}_{\text{Ozone Reaction}}$$

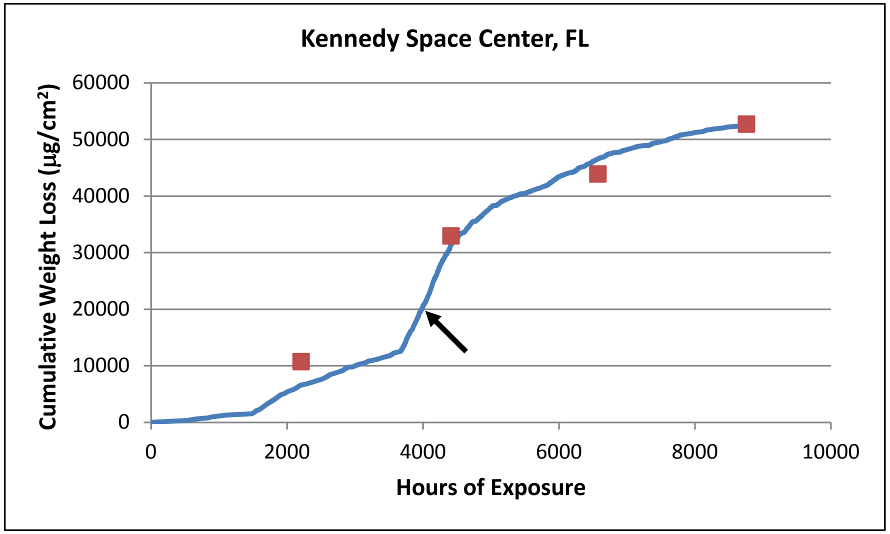
AFRL SERDP Project - Cumulative Damage Model Results



AISI 1010 Steel Hourly Corrosion Rate Predictions for Kennedy Space Center, FL (midnight 12-13-05 to midnight 12-14-05)



AISI 1010 Steel Cumulative Corrosion Rate Predictions for Kennedy Space Center, FL (midnight 12-13-05 to midnight 12-14-05)



Comparison of AISI 1010 Steel Corrosion Test Points and Associated Predictions

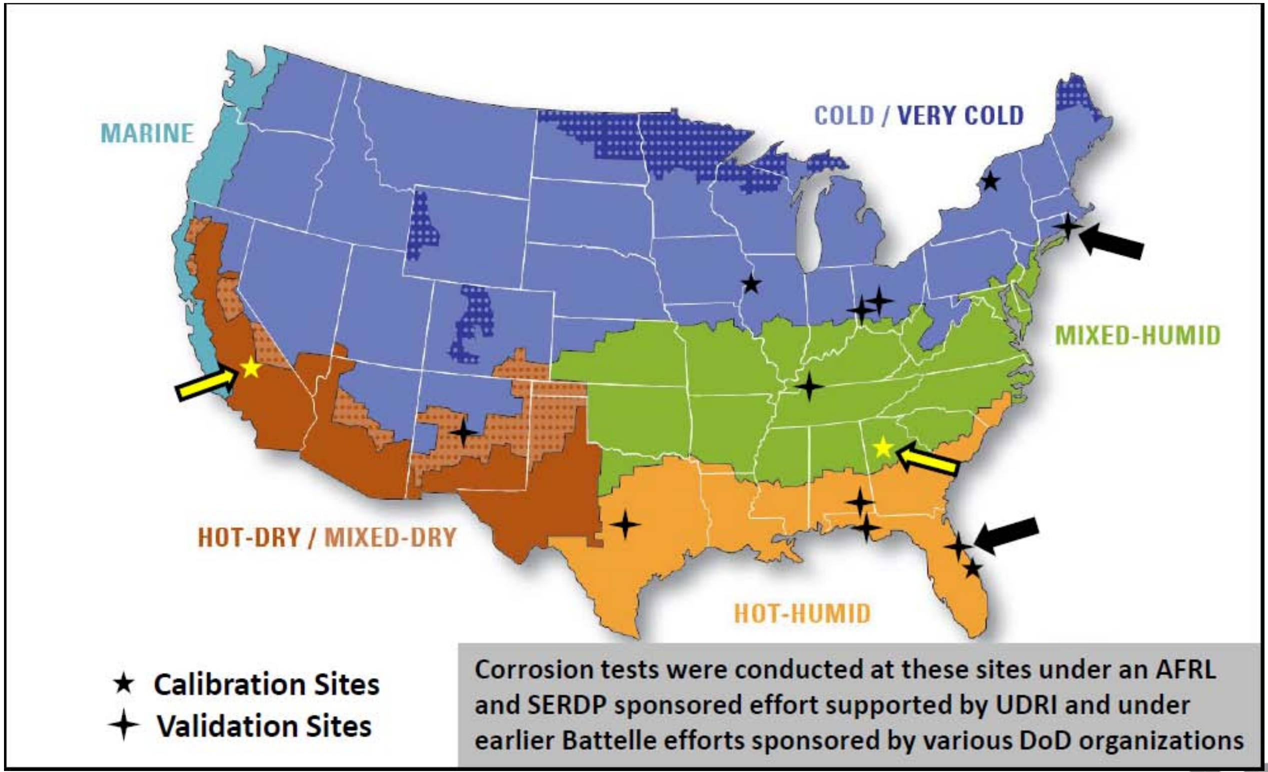
AFRL SERDP – Outdoor Test Site Locations

Calibration/Validation Sites

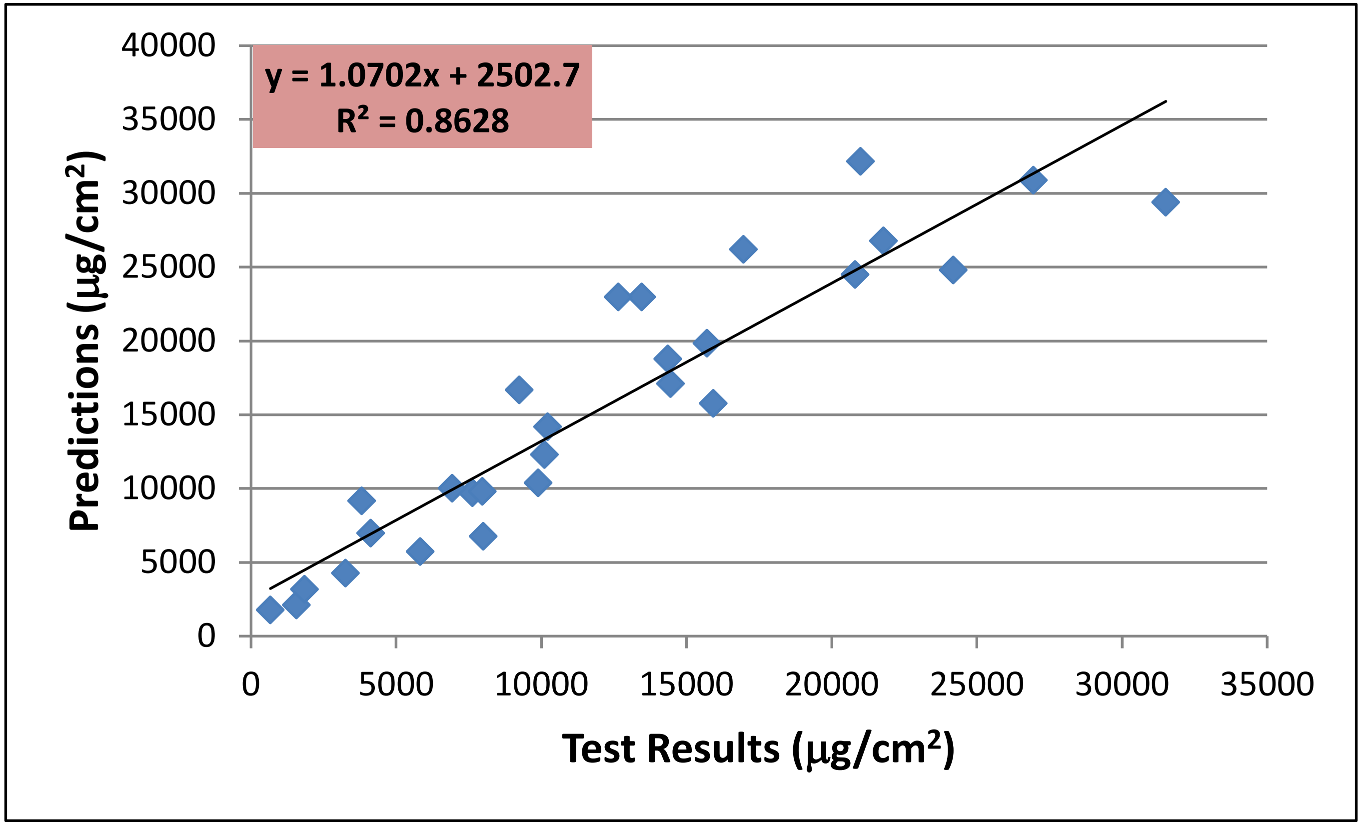
• Data from four different locations with diverse conditions was used to initially calibrate candidate models… later reduced to three sites

• Candidates were validated by applying them to independent proxy data for locations not used for calibration

– Final model was validated using data from seven different sites in four different climate zones



AFRL SERDP Project - Cumulative Damage Model Results



R^2 value of 0.86 is higher than any published atmospheric corrosion rate prediction model intended for application at locations with diverse environmental conditions

AFRL Phase I 2014.1 SBIR Topic

2014.1 SBIR topic AF141-164, “Programmable Accelerated Environmental Test System for Aerospace Materials”

Combined environmental effects:

- Salt fog (NaCl, $CaCl_2$, etc.)
- Gas exposure (ozone, CO_2, etc.)
- Artificial sunlight-UV weathering
- Temperature and humidity cycling
- Dynamic mechanical loading

Four contracts awarded; final reports due ~Feb 2015:

- **Systems and Materials Research Corporation**
- **Luna Innovations**
- **SAFE Engineering**
- **Mainstream Engineering**

Goal: commercialization of apparatus, test method development, inclusion in MIL Specifications (e.g. MIL-PRF-32239, “COATING SYSTEM, ADVANCED PERFORMANCE, FOR AEROSPACE APPLICATIONS”)

Programmable Accelerated Environmental Test System for Aerospace Materials

Expected Advantages:

- **Improved correlation between test results and service performance**
- **Failure modes similar to those observed in service**
- **Accelerated test times compared to outdoor exposure**
- **Ability to simulate environmental conditions for specific operational and test locations (e.g. Hickam AFB, Daytona Beach)**
- **Programmable and fully automated**

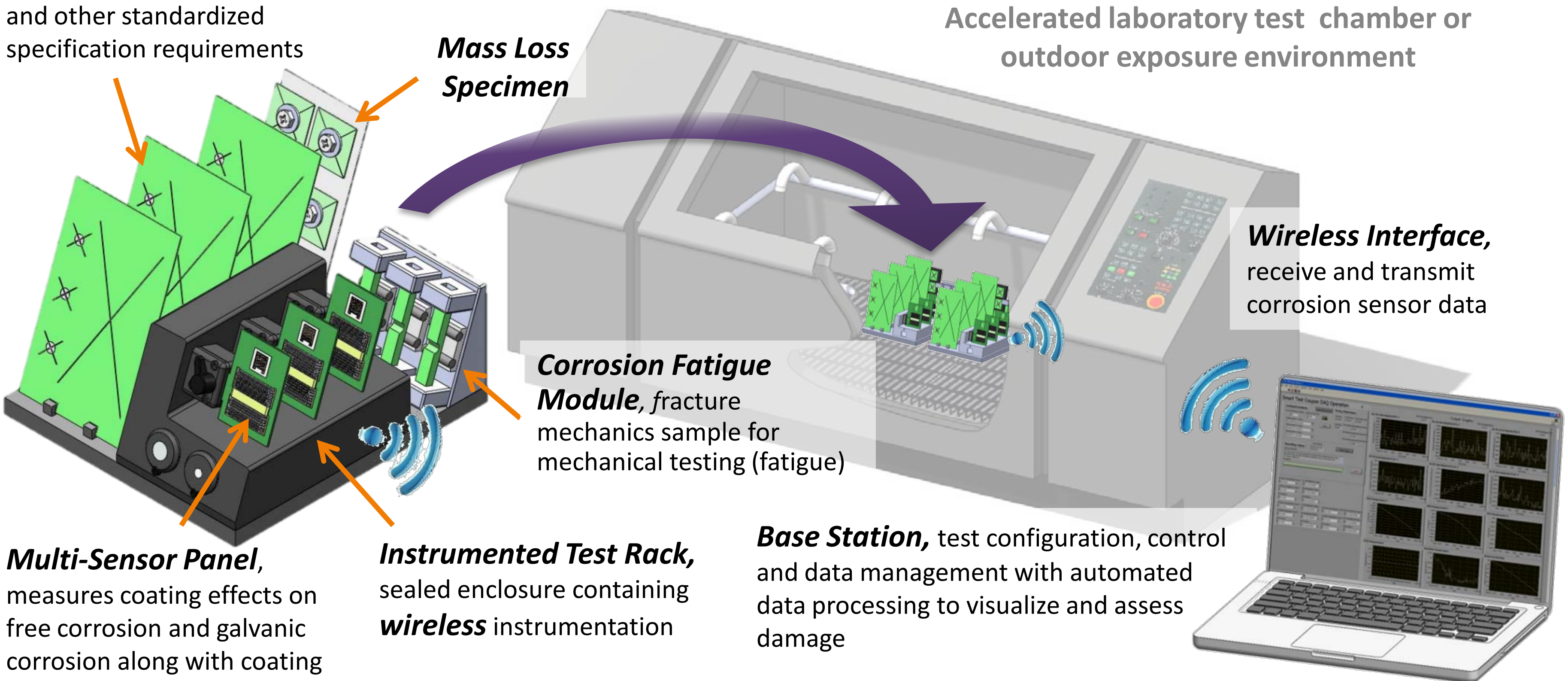
Existing test standards can be modified and tailored to specific applications

- **Example: ASTM D7869 – (Xenon Arc UV + water spray)**

Step Number	Step Minutes	Function	Irradiance Set Point[A] at 340 nm $W/(m^2 \cdot nm)$	Black Panel Temperature Set Point[A]	Chamber Air Temperature Set Point[A]	Relative Humidity Set Point[A]
1	240	dark + spray	—	—	40°C	95 %
2	30	light	0.40	50°C	42°C	50 %
3	270	light	0.80	70°C	50°C	50 %
4	30	light	0.40	50°C	42°C	50 %
5	150	dark + spray	—	—	40°C	95 %
6	30	dark + spray	—	—	40°C	95 %
7	20	light	0.40	50°C	42°C	50 %
8	120	light	0.80	70°C	50°C	50 %
9	10	dark	—	—	40°C	50 %
10	Repeat subcycle steps 6 to 9 (shown in bold) an additional 3 times (for a total of 24 h = 1 cycle).					

WR-ALC SBIR Phase II.2 and SBIR CRP Project - Luna Innovations

Corrosion and Coating Evaluation (CorRES) System



POC: David Ellicks, AFRL/AFCPCO

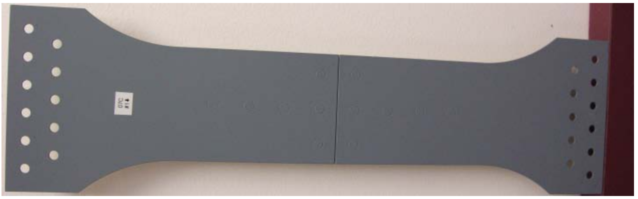
AFRL Structural Component Corrosion Simulation (SCCS)

- Driven by ASIP requirements for fleet corrosion management, especially with emerging environmentally compliant materials and processes

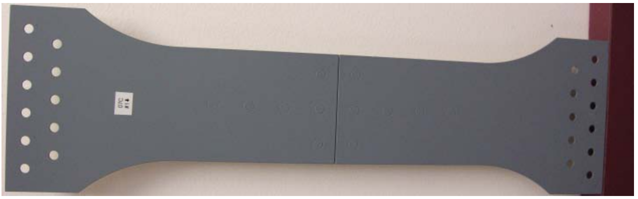
- Specimen will have representative materials and geometries

- Test will combine stress with simulated aircraft environment that includes T, RH%, wet/dry cycles, UV, and background gases (ozone, CO_2, etc.)

- Deliverable will be JTP that prescribes:
  - Specimen design and construction materials
  - Finish system – organic coatings, sealants, CPCs, etc.
  - Laboratory exposures to simulated environments
  - Non-destructive inspection during testing
  - Teardown and analysis protocol



AFRL Structural Component Corrosion Simulation (SCCS) – Baseline Study

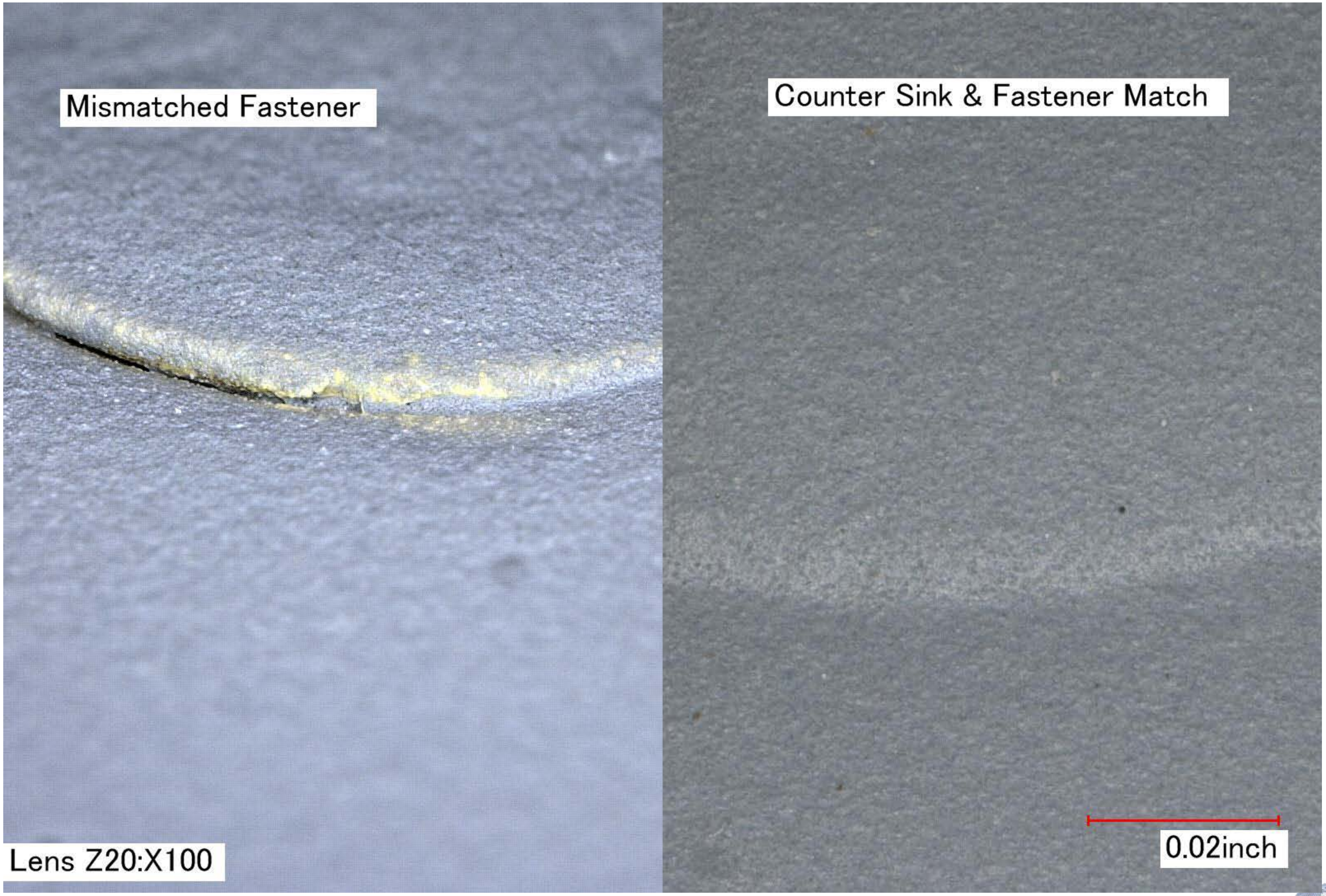


- Baseline study: representative large airframe legacy aircraft materials selected; “worst case” condition
  - Bare 7075-T6 skin, stiffener, splice plate
  - Cd-plated steel fasteners
  - Dry-installed fasteners; no fay surface sealants or CPCs
  - Chromated and non-chromated coating systems
- Specimens subjected to alternating ASTM B117 salt fog, UV (500 hrs, UVB), axial cyclic loading with temp. cycling -65°F to 85°F
- All relevant control groups (64 total specimens)
- NDI during testing with complete teardown analysis

Fatigue loading:

- R = 0.05, f = 5 Hz
- 11.7 ksi peak stress for 5,000 cycles per block
- 2 full temperature cycles per block (-65°F to 85°F)
- Purpose of loading is to stress the coating to initiate corrosion

AFRL Structural Component Corrosion Simulation (SCCS)



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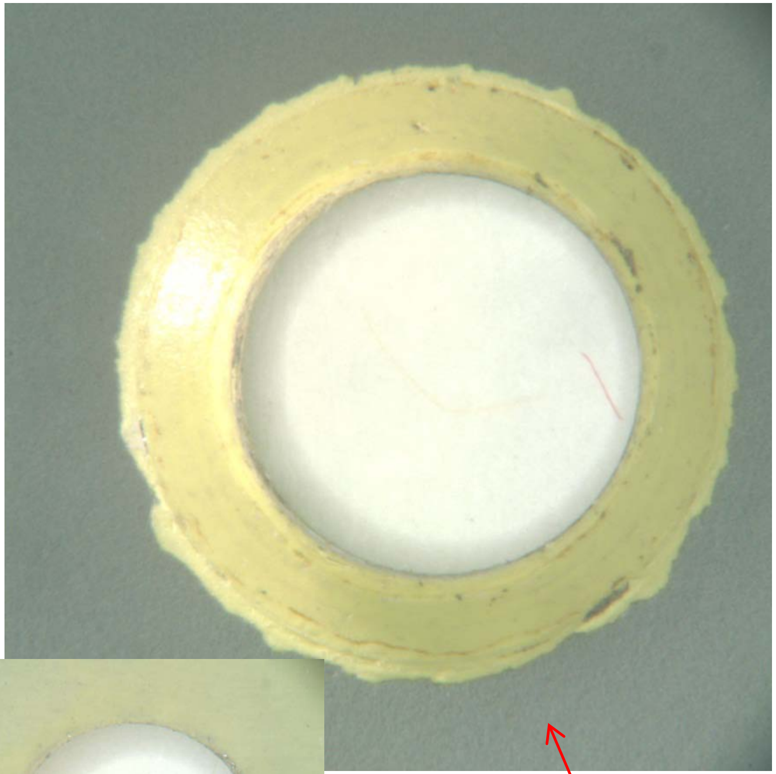
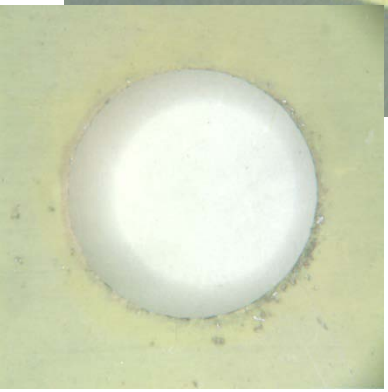
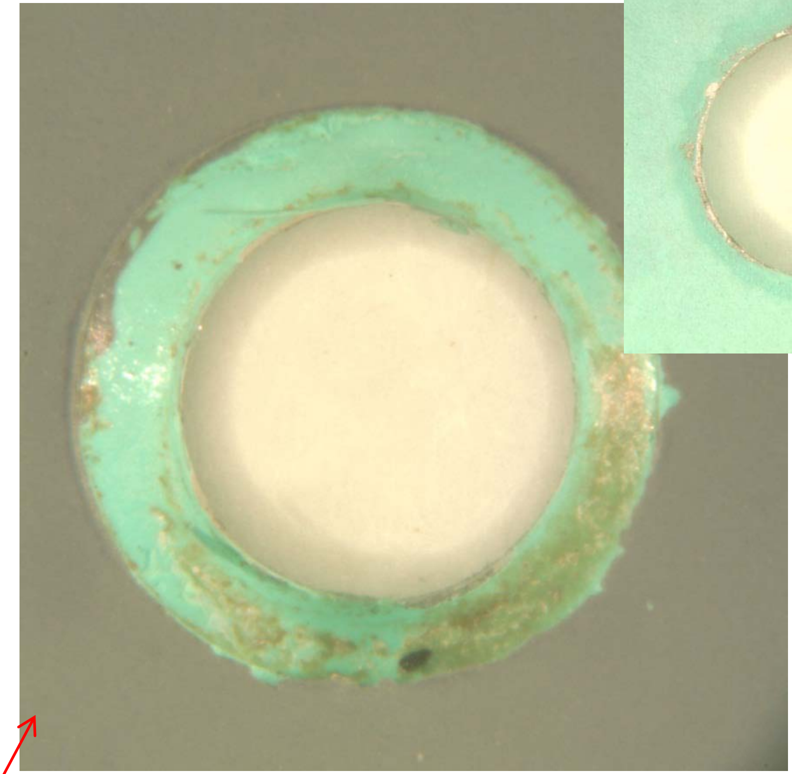
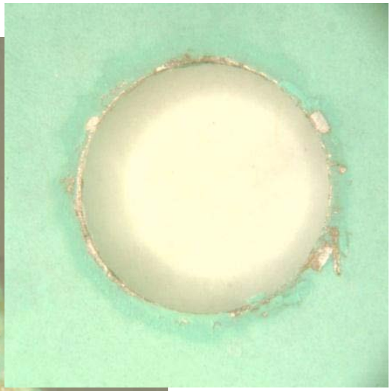
AFRL Structural Component Corrosion Simulation (SCCS)









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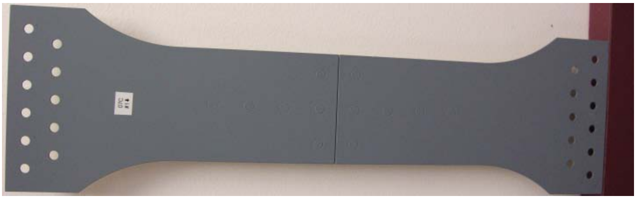
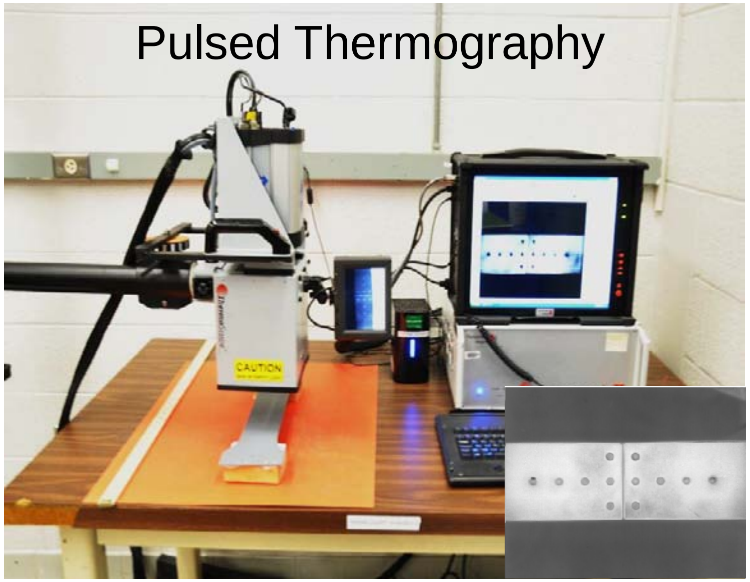
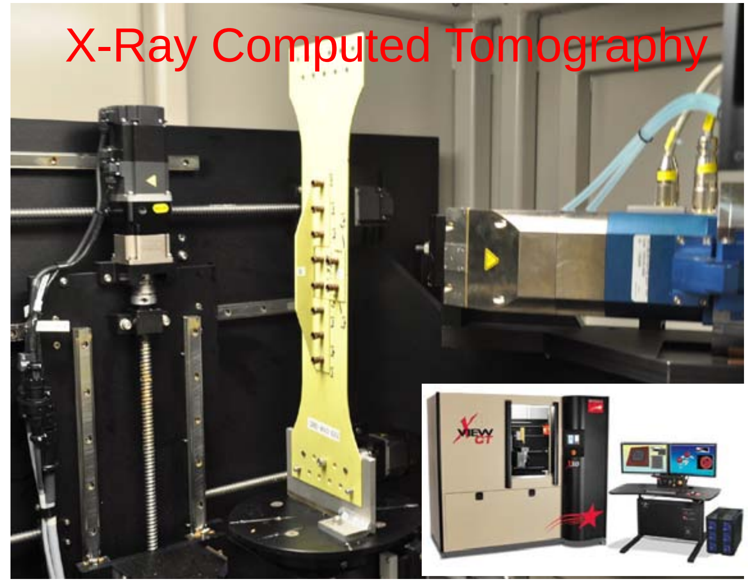
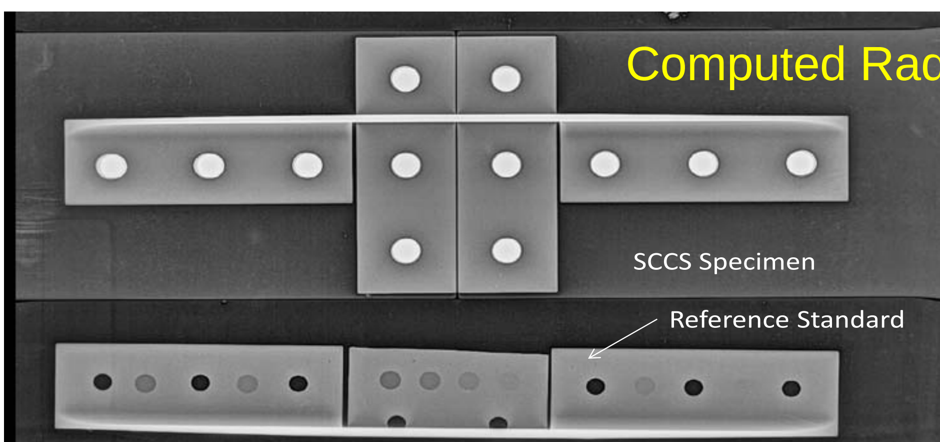
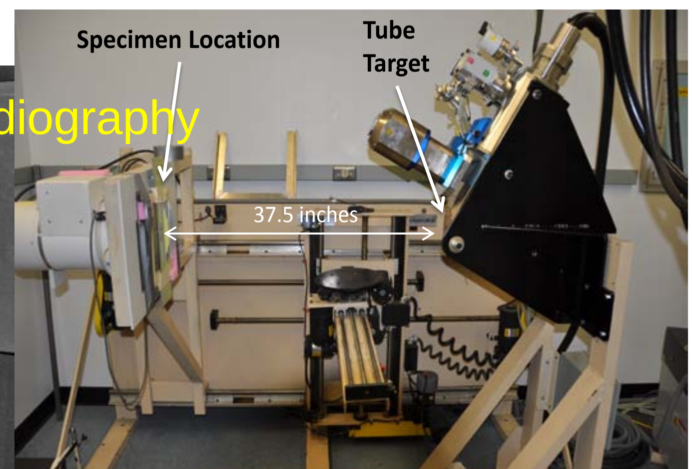


Non-Destructive Inspection



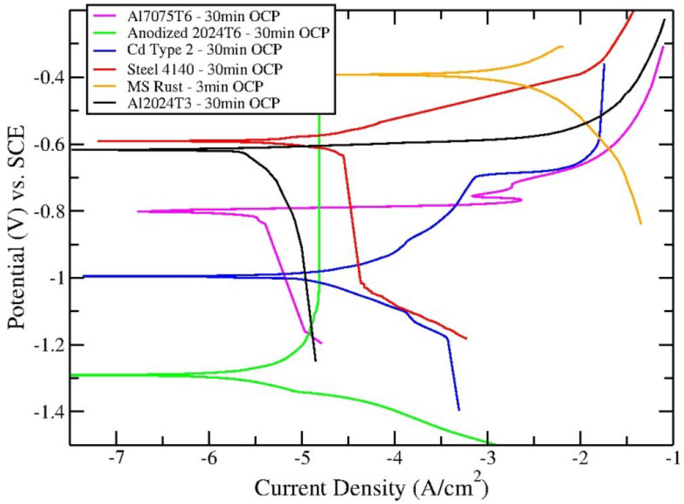


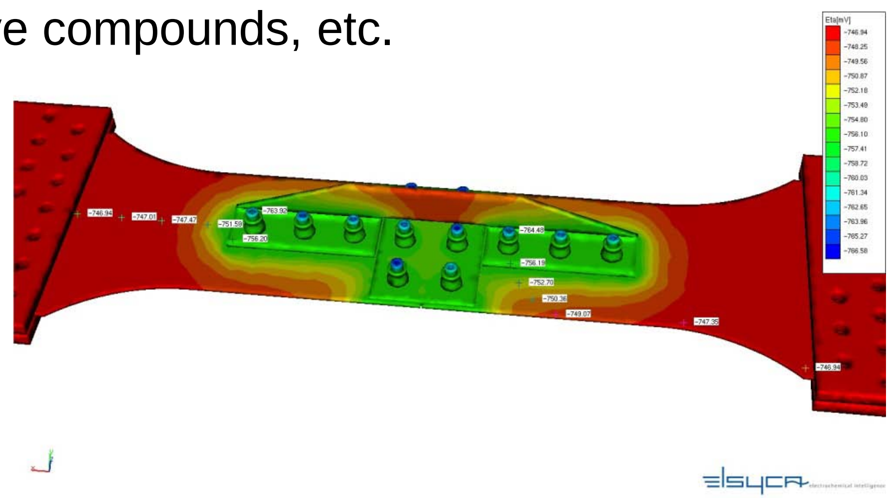




Corrosion modeling

- Commercially available software (e.g. GalvanicMaster) uses finite element models and electrochemical data input and can provide prediction of initial corrosion rates for a metallic structure assembly, given a set of assumptions
- AFRL 2014.1 Phase I SBIR "Galvanic Corrosion Prediction of Aircraft Structures" to expand capability to aluminum structure/composite joints with fasteners
- Eventual goal is to allow for dynamic prediction and include coatings, sealants, corrosion preventative compounds, etc.





Conclusions

- **Air Force need/requirement for rapid (< 1 month) evaluation of aircraft corrosion protection schemes to comply with MIL-STD-1530C and hazardous material elimination demands**
- **No <u>methods</u> or <u>test apparatus</u> exist that can simulate service conditions/accurate degradation mechanisms in the laboratory!**
- **Multiple AFRL projects/programs addressing this gap**
- **Desired end state: accurate forecast of service performance of corrosion protection scheme via improved test protocols (informed by corrosion/coatings science and computational models).**

Backup

DoD Corrosion Forum - Accelerated Corrosion Testing Working Group

- Part of DoD Corrosion Forum
  - DoD Corrosion Policy and Oversight Office (under OUSD AT&L)
  - Meet 3-4 times annually
  - Tri-service participation
- Goal is to create a product: White Paper Summary that includes:
    - Define the current state-of-the-art of subject
    - Identify gaps and needs, and recommend next steps
    - Grand vision – consider the level of technical maturity or complexity of the product necessary to solve “the” DoD problem
- Five year plan detailing an investment strategy

SERDP - Cumulative Damage Modeling Approach – Dave Rose PhD Dissertation

- Cumulative corrosion damage models (developed using computer simulations) consider actual variable environmental conditions…
  - Approach is analogous to random amplitude fatigue modeling
- Optimized model resulting from PhD research program focused on AISI 1010 Steel
  - Non-optimized models have also been created for copper and 2024, 6061, and 7075 aluminum alloys
    - Annual cumulative predictions (for all materials) were made for over 110 C-5 deployment locations world-wide
- Ongoing internship program sponsored by the DoD HPC program is using a supercomputer to further optimize all models
- Cumulative predictions not limited to single locations
  - The same approach could be used to estimate environmental attack on aircraft that fly between bases
    - Would need dates and times on the ground to account for diurnal and seasonal temperature changes and related changes to humidity levels

Cumulative Damage Model for Prediction of Atmospheric Corrosion

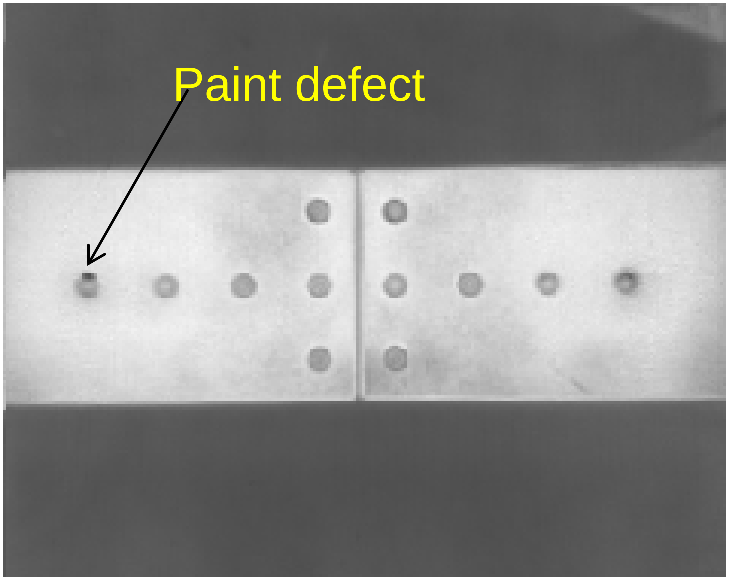
$$K_i = \exp\left(\frac{\Delta H}{kT}\right)[A_{CL}T^{\alpha CL} f_{Cl}(T,RH)f(T,Cl) + A_{SO2}T^{\alpha SO2} f_{SO2}(T,RH)f(T,SO_2) +$$
$$A_{O3}T^{\alpha O3} f_{O3}(T,RH)f(T,O_3)$$

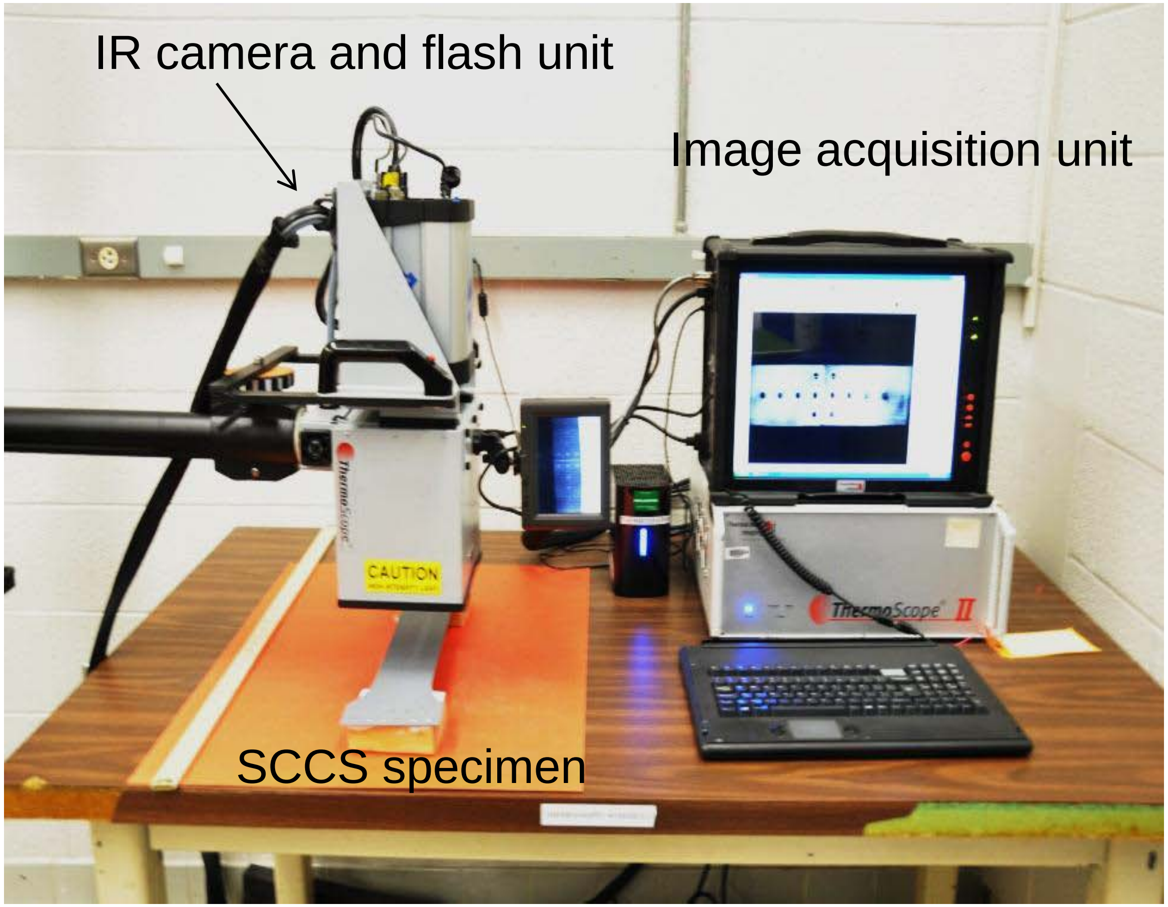
Model Component	Description	Units
K_i	Hourly corrosion rate	µg/cm^2
A_{Cl}	Scaling factor for the chloride reaction	µg/cm^2
A_{SO2}	Scaling factor for the SO_2 reaction	µg/cm^2
A_{O3}	Scaling factor for the ozone reaction	µg/cm^2
αCl	Temperature adjustment exponent used for the chloride reaction	nondimensional
αSO_2	Temperature adjustment exponent used for the SO_2 reaction	nondimensional
αO_3	Temperature adjustment exponent used for the ozone reaction	nondimensional
T	Temperature	Kelvin (K)
ΔH	Activation energy for the single activation energy formulation	eV/K
K	Boltzmann constant (=8.6173 x 10^{-5} eV/K)	eV/K
$f_{Cl}(T,RH)$	Temperature-Relative Humidity shape function for the chloride reaction.	nondimensional
$f_{SO2}(T,RH)$	Temperature-Relative Humidity shape function for the SO_2 reaction.	nondimensional
$f_{O3}(T,RH)$	Temperature-Relative Humidity shape function for the ozone reaction.	nondimensional
$f_{Cl}(T,Cl)$	Temperature-Contaminant shape function for the chloride reaction. Calibrated using chloride deposition measurements (mass per unit volume of rainwater*)	nondimensional
$f_{SO2}(T,SO_2)$	Temperature-Contaminant shape function for the SO_2 reaction. Calibrated using hourly gaseous measurements (ppm) measured by automated air pollution monitoring systems.	nondimensional
$f_{O3}(T,O_3)$	Temperature-Contaminant shape function for the ozone reaction. Calibrated using hourly gaseous measurements (ppm) measured by automated air pollution monitoring systems.	nondimensional

DoD Corrosion "Gap" Analysis

- Air Force materials and processes subject matter experts met Sep 2011 to discuss corrosion
- Identified gaps/needs:
    - Ability to translate top-level service life (hours and years in service) and sustainment requirements into selection of materials, finish systems, etc. that withstands competing pressures during design
    - Well defined and agreed-to accelerated test methods and accept/reject criteria for corrosion evaluation for a range of environments and service life requirements
    - DoD-wide evaluation & recommendation/approval for cross-cutting material substitutions, process changes, such as:
        - Material substitutions: chromated primer, chromic acid anodize, chrome plating, cadmium plating
        - Process changes: paint removal (chemical, plastic media, laser, etc.)

Pulsed Thermography

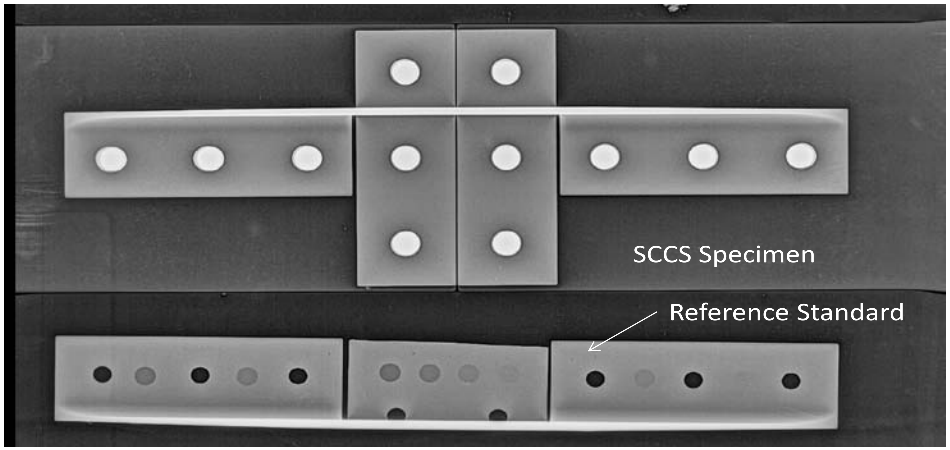


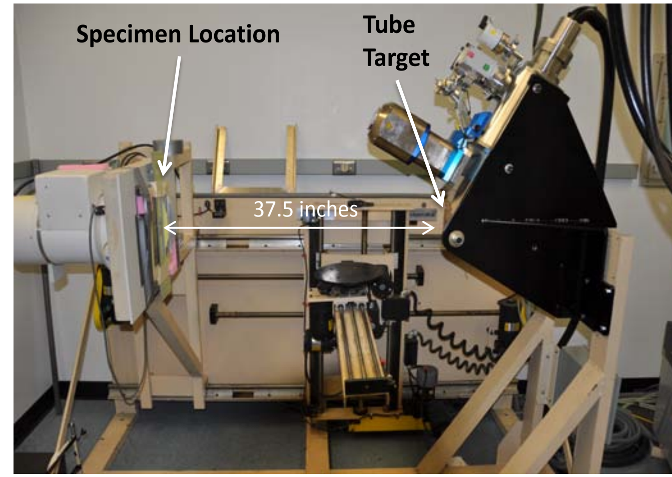


Pulsed Thermography– Uses pulsed thermal excitation and infrared camera to image the coated surface. Detects corrosion formation at coating to substrate interface.

Computed Radiography

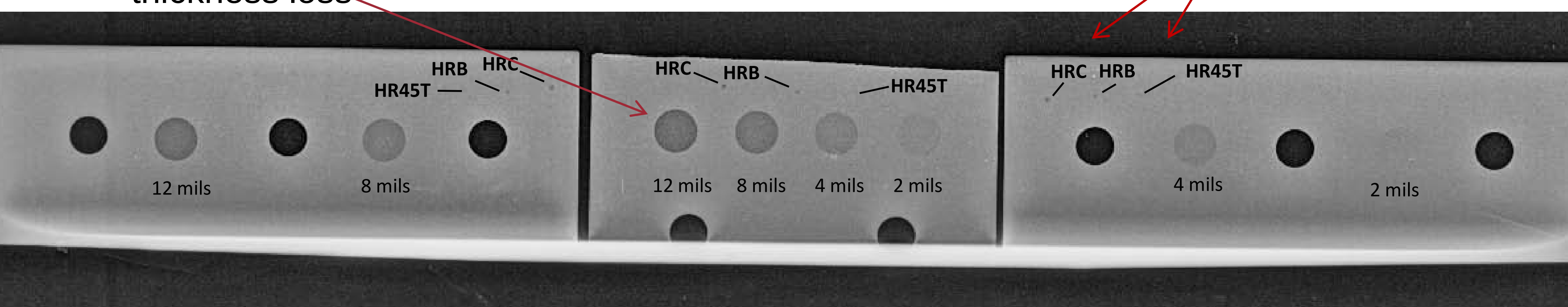
Computed Radiography– X-ray 2D digital imaging to identify inter-layer material loss and provide rough estimates of thickness loss and area.





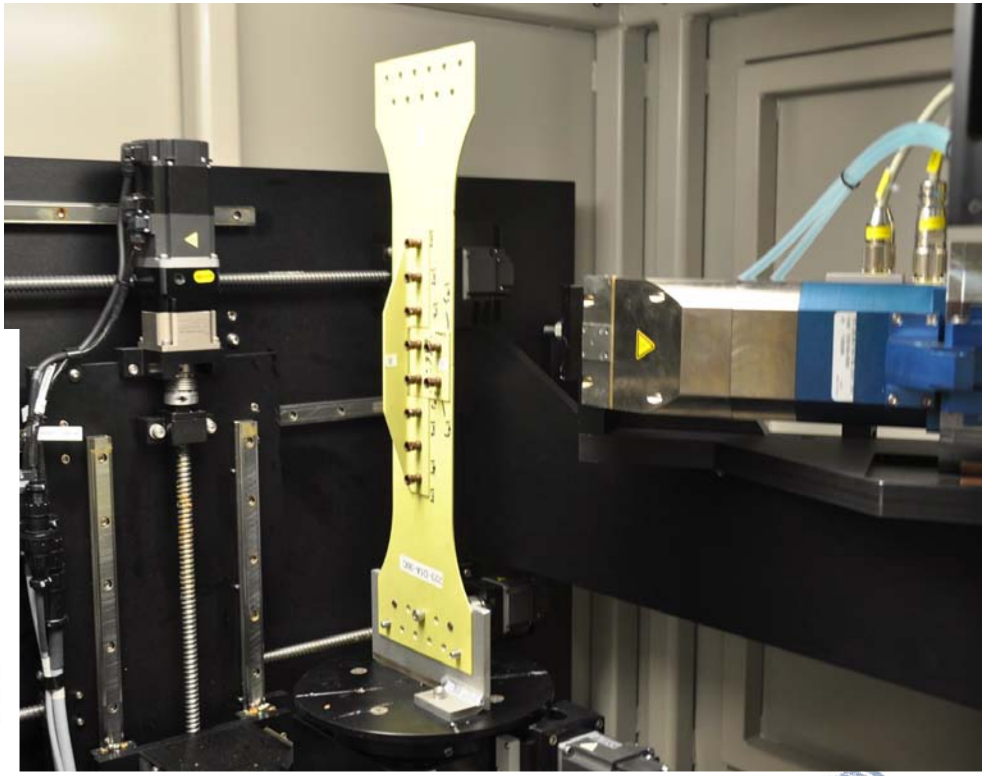
Simulated pits (hardness tester indents)

Flat bottom holes to calibrate thickness loss



AFRL X-Ray Computed Tomography

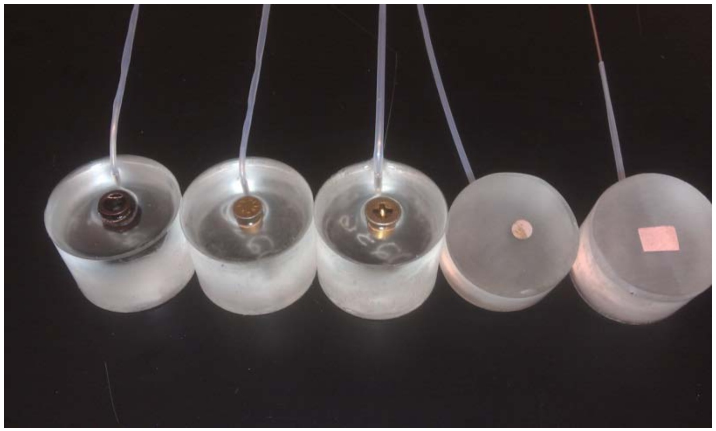
Computed Tomography (CT) - High resolution 3D imaging of material loss. Anticipated to provide accurate measure of thickness loss within individual layers of the SCCS specimens without disassembly.

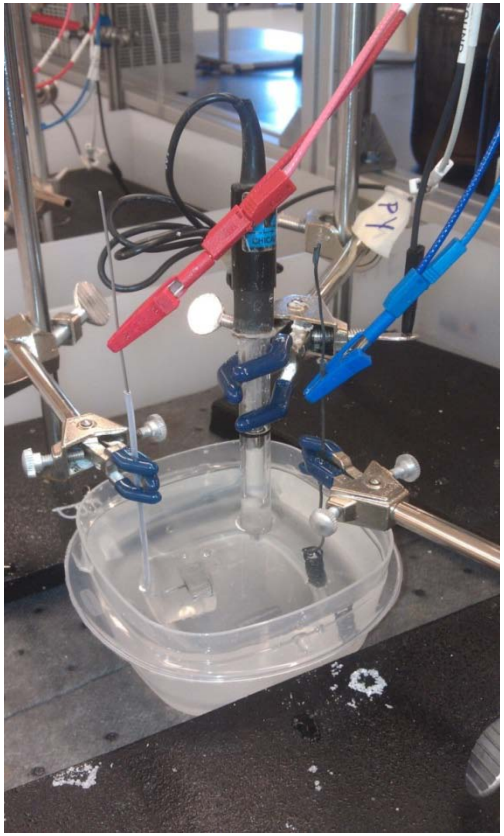


AFRL X-Ray Computed Tomography

- North Star Imaging (NSI) X50 CT System (Enclosed cabinet)
  - Ability to move detector closer or further away from tube/stage
  - Tube is Fixed
  - Scanning envelope for stage: X (up/down), Y (left/right), Tilt (+20 / -10^0 ; 20 to detector / 10 to source), and Rotate (Continuous 360^0)
- FeinFocus FXE 225.48 Micro-focus X-ray Tube
  - 225 kV
  - 3 mA
- Perkin Elmer XRD 0822 AO Digital X-Ray Flat Panel Detector
  - Field of View: 8” x 8”
- Stage
  - Diameter: 8 inches
  - Load Limit: 25 lbs.
- System Resolution
  - ~ 1 μm voxel size (depends on distance to x-ray tube, size of part)
  - ~ 4 μm voxel size (best resolution we have achieved on a component)

Electrochemical Setup





<u>Working Electrode</u>

- Mounted Sample

<u>Counter Electrode</u>

- Platinum

<u>Reference Electrode</u>

- SCE .241V vs. SHE